CLAIMS

1. A method for preparing polyorganosiloxanes (POSs) by ring-opening and/or redistribution polymerization of POSs, in the presence of a catalyst (C), characterized in that this catalyst (C) comprises at least one carbene.

2. The method as claimed in claim 1, characterized in that the carbene of the catalyst (C) comprises two nonbonding electrons, which are in the singlet or triplet, preferably singlet, form.

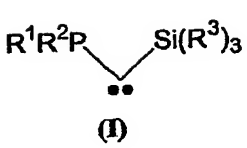
3. The method as claimed in either one of the preceding claims, characterized in that the carbene(s) of the catalyst (C) has (have) a general structure represented by formula **(I°)**:

(I°)

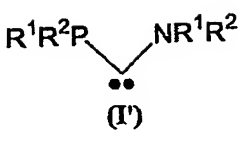
in which:

- X and Y are independently chosen from the group comprising: S, P, Si, N and O;
- X and Y are optionally substituted;
- X and Y can be connected via at least one optionally substituted five-, six- or seven-membered hydrocarbon-based ring; or a five-, six- or seven-membered heterocycle comprising one or more hetero atoms chosen from the group comprising: S, P, Si, N and O, and optionally substituted.

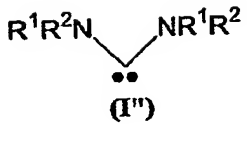
4. The method as claimed in claim 3, characterized in that the carbene(s) of the catalyst (C) has (have) a general structure represented by formula **(I)**, **(I')** or **(I'')**:



(I)



(I')

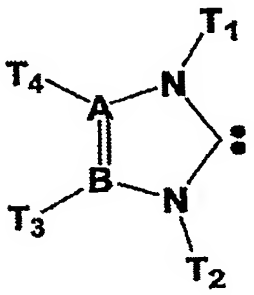


(I")

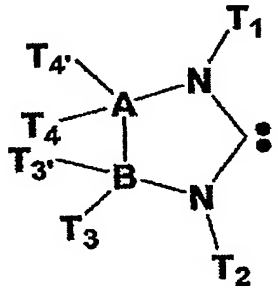
in which:

- R^1, R^2 and R^3, which may be identical or different, independently represent an alkyl group; an optionally substituted cycloalkyl group; an optionally substituted aryl group; or
- the groups R^1 and R^2 can together form an optionally substituted five- or six-membered hydrocarbon-based ring; or else a five- or six-membered heterocycle comprising one or more hetero atoms chosen from the group comprising: S, P, Si, N and O, and optionally substituted.

5. The method as claimed in claim 3, characterized in that the carbene(s) of the catalyst (C) correspond(s) to formula **(II)** or **(II')**:



(II)



(II')

in which:

- A and B independently represent C or N, it being understood that:
  - in formula **(II)**, when A represents N, then T4 is not present, and when B represents N, then T3 is not present;
  - in formula **(II')**, when A represents N,

then T4 or T4' is not present, and when B represents N, then T3 or T3' is not present;

- T3, T3', T4 and T4' independently represent a hydrogen atom; an alkyl group; a cycloalkyl group optionally substituted with alkyl or alkoxy; an aryl group optionally substituted with alkyl or alkoxy; an alkenyl group; an alkynyl group; or an arylalkyl group in which the aryl part is optionally substituted with alkyl or alkoxy; or
- T3 and T4 can form, together and with A and B when the latter each represent a carbon atom, an aryl, it being understood that, in this case, T3' and T4' are not present;
- T1 and T2 independently represent an alkyl group; an alkyl group optionally substituted with alkyl; an alkyl group that is perfluorinated or optionally substituted with a perfluoroalkyl group; a cycloalkyl group optionally substituted with alkyl or alkoxy; an aryl group optionally substituted with alkyl or alkoxy; an alkenyl group; an alkynyl group; or an arylalkyl group in which the aryl part is optionally substituted with alkyl or alkoxy; or

T1 and T2 independently represent a monovalent radical of formula **(V)** below:

-V1-V2 **(V)**

in which:

- V1 is a saturated or unsaturated, hydrocarbon-based divalent group, preferably an optionally substituted linear or branched C_1-C_{10} alkylene,
- V2 is a monovalent group chosen from the group of the following substituents:
  - alkoxy, $-OR^a$ with R^a corresponding to hydrogen, alkyl or aryl;
  - silyl, $-Si(OR^b)_x(R^c)_{3-x}$ with R^b corresponding

to hydrogen, alkyl, silyl or siloxanyl, R^c corresponding to alkyl or aryl, and x being an integer between 0 and 3;

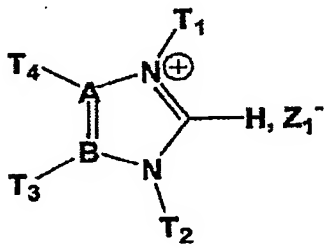
- ♦ amine, preferably $-N(R^a)_2$ with R^a corresponding to hydrogen, alkyl or aryl; or

- the substituents T1, T2, T3, T3', T4 and T4' can form, in pairs, when they are located on two adjacent vertices in formulae **(II)** and **(II')**, a saturated or unsaturated hydrocarbon-based chain.

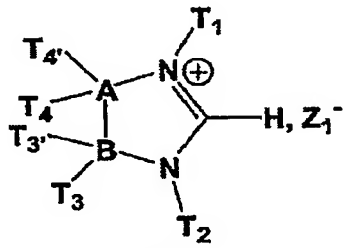
6. The method as claimed in any one of the preceding claims, characterized in that the carbene(s):
   - is (are) prepared separately,
   - and/or is (are) generated in situ from at least one precursor.

7. The method as claimed in claim 6, characterized in that the precursor(s) is (are) a salt (salts) corresponding to the carbene(s), which is (are) reacted with at least one base, so as to generate the carbene(s) in situ.

8. The method as claimed in claim 6, characterized in that the corresponding salt(s) is (are) one (or more) corresponding heterocyclic salt(s) of general formula **(III)** or **(III')**:



(III)



(III')

in which:

- A, B, T1, T2, T3, T3', T4 and T4' are as defined in claim 6;
- Z1 independently represents an anion derived from a Brönsted acid (protic acid) preferably chosen from the group comprising:
  - carboxylic acids of formula G_o-COOH in which G_o represents an alkyl, and advantageously a C_1-C_{22} alkyl; an aryl, advantageously a C_6-C_{18} aryl optionally substituted with one or more C_1-C_6 alkyls;
  - sulfonic acids of formula G_o-SO_3H in which G_o is as defined above;
  - phosphoric acids of formula G_o-PO_3H in which G_o is as defined above;
  - the following inorganic acids: HF, HCl, HBr, HI, H_2SO_4, H_3PO_4, $HClO_4$ and HBF_4 taken on their own or in combination with one another;
  - and mixtures thereof.

9. The method as claimed in any one of the preceding claims, characterized in that it is carried out, by homogeneous catalysis, in a liquid reaction medium in which are at least partially solubilized the catalyst (C) based on carbene(s) and/or its precursor(s) and the initial POSs, and optionally at least one base.

10. The method as claimed in any one of the preceding claims, characterized in that the solubility of the catalyst (C) based on carbene(s) and/or its precursor(s) is controlled by means of at least one solubilization helper and/or using one (or more) carbene(s) substituted with at least one appropriate group.

11. The method as claimed in any one of the preceding claims, characterized in that it is essentially

carried out at a temperature T (°C) such that:

$$T \leq 200$$

preferably $100 \leq T \leq 150$

and even more preferably $T \leq 100$.

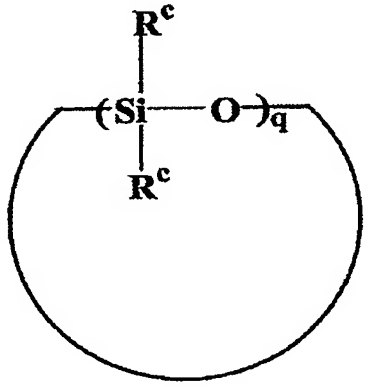
12. The method as claimed in claim 1, characterized in that the concentration of catalyst [C] (in mol per 100 g of initial POSs) in the reaction medium is such that:

$$[C] \leq 1$$

preferably $10^{-5} \leq [C] \leq 10^{-1}$

and even more preferably $10^{-5} \leq [C] \leq 10^{-3}$.

13. The method as claimed in any one of the preceding claims, characterized in that the initial POSs comprise cyclic POSs (POScy), preferably chosen from those corresponding to general formula **(XI)** below:



(XI)

in which:

R^c represents hydrogen or an alkyl or aryl radical

and $3 \leq q \leq 12$.

14. The method as claimed in any one of the preceding claims, characterized in that the initial POSs are linear and are preferably selected from those of

general formula **(XII.1)**:

$$R^a\text{-}[(R^b)_2Si\text{-}O\text{-}]_p\text{-}Si(R^b)_2\text{-}R^a \qquad \textbf{(XII.1)}$$

in which:

- R^a independently represent a hydroxyl, an alkyl or an aryl, optionally comprising one or more hetero atoms and optionally substituted with halogens,
- R^b independently represent an alkyl or an aryl, optionally comprising one or more hetero atoms and optionally substituted with halogens,
- and $p \geq 2$.

15. The method as claimed in claim 14 and, optionally, at least any one of the other preceding claims, characterized in that the final POS/POScy ratio in the reaction medium is greater than 85/15, preferably greater than or equal to 90/10, and even more preferably greater than or equal to 95/5.

16. The method as claimed in any one of the preceding claims, characterized in that the following are used:

- o POSs substituted with catalytic functions able to generate carbenes, and preferably catalytic functions derived from products of formula **(I°)**, **(I)**, **(I')**, **(II)**, **(II')**, **(III)** or **(III')** as defined in the preceding claims;
- o and/or silanes of formula:

$$(OR^*)_{4-a}Si(R^c)_a$$

in which:

- R^c is a catalytic function able to generate a carbene, and preferably a catalytic function derived from a product of formula **(I°)**, **(I)**, **(I')**, **(II)**, **(II')**, **(III)** or **(III')** as defined in the preceding claims,
- R^* is an alkyl,

- a = 1 to 3.

17. A composition that can be used in particular for the preparation of polyorganosiloxanes (POSs) by polymerization and/or redistribution of POSs, characterized in that it comprises:
* linear or nonlinear POSs and/or cyclic POSs (POScy);
* a catalyst (C) comprising at least one carbene in which the two nonbonding electrons are preferably in the singlet form; with the exclusion of any catalyst formed by at least one metal(s)/carbene(s) complex, in particular Pt/carbene(s);
* optionally, at least one solvent;
* and, optionally, linear POSs, for example polydialkyl (e.g. methyl)siloxanes MD_pM with p = 0 to 20, preferably 0 to 10, and more preferably p = 0: namely, disiloxanes, for example those belonging to the group comprising hexamethyldisiloxane (M2), vinylated M2 and hydrogenated M2.

18. The composition as claimed in claim 17, characterized in that the catalyst (C) is as defined in claims 2 to 8.

19. The composition as claimed in claim 18 or 19, characterized in that the initial POSs are as defined in claim 13 or 14.

20. The composition as claimed in any one of claims 17 to 19, characterized in that the catalyst (C) is generated in situ from at least one precursor chosen from the group comprising one or more salt(s) corresponding to the carbene(s), capable of reacting with at least one base, so as to generate the carbene(s) in situ.

21. The composition as claimed in any one of claims 17 to 20, characterized in that it comprises at least one solubilization helper and/or the carbene(s) is (are) substituted with at least one solubilizing group.

22. The composition as claimed in any one of claims 19 to 21, characterized in that the concentration of catalyst [C] (in mol per 100 g of initial POSs) in the reaction medium is such that:

$$[C] \leq 1$$

preferably $10^{-5} \leq [C] \leq 10^{-1}$

and even more preferably $10^{-5} \leq [C] \leq 10^{-3}$.

23. A silicone composition, characterized in that it comprises:

→ at least one POS obtained by polymerization and/or redistribution of POSs;

→ at least one residue of catalyst (C) as defined in the preceding claims.

24. A silicone composition comprising at least one POS obtained by ring opening and then polymerization and/or redistribution of POSs, and in particular of POScy, characterized by a final POS/POScy ratio of greater than 85/15, preferably greater than or equal to 90/10, and even more preferably greater than or equal to 95/5.

25. POSs substituted with catalytic functions able to generate carbenes, preferably derived from products of formula **(I°)**, **(I)**, **(I')**, **(II)**, **(II')**, **(III)** or **(III')** as defined in the preceding claims.

26. Silanes of formula:

$$(OR^*)_{4-a}Si(R^c)_a$$

in which:

- o R^c is a catalytic function able to generate a carbene, and preferably a catalytic function derived from a product of formula **(I°)**, **(I)**, **(I')**, **(II)**, **(II')**, **(III)** or **(III')** as defined in the preceding claims,
- o R* is an alkyl,
- o a = 1 to 3.

27. Use of carbene(s) as defined in the preceding claims, as a catalyst or cocatalyst in the preparation of POSs by polymerization and/or redistribution of POSs.